Modelling of Kinetic Interface Sensitive Tracers for Two-Phase Systems

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Abstract. This article presents a mathematical model for interface sensitive tracer transport used for the evaluation of the interface between two fluid-phases (i.e. CO_2 and brine) with general applicability in a series of engineering applications: oil recovery, vapour-dominated geothermal reservoirs, contaminant spreading, CO_2 storage, etc. Increasing the CO_2 storage efficiency in brine deep geological formations requires better injection strategies to be developed which could be accomplished with better tools for quantification of the fluid-fluid interfaces. The CO_2 residual and solubility trapping are highly influenced by the interfaces separating the phases. An increase in the interface area is expected to produce an increase in the solubility trapping. However, standard multi-phase models do not account for the specific fluid-fluid interface area. A new class of reactive tracers is used for the characterization of interfacial areas between supercritical CO_2 and brine. The tracer is injected in the CO_2 and migrates to the interface where it undergoes a hydrolysis reaction in contact with water. A mathematical model is constructed based on volume-averaged properties (saturation, porosity, permeability, etc.) at the macroscale. The fluid phases are described with an extended form of the Darcy equation based on thermodynamic principles and complemented with relations for relative permeability and saturation and a specific equation for interfacial area. The kinetic mass transfer effects between the two phases are highly dependent on the interface area, and are captured with an approach introduced by [1]. The mathematical model is tested with a simple numerical example.

Keywords: two phase flow in porous media, kinetic interface sensitive tracers, specific interfacial area.

1 Motivation

Flow, transport and phase transfer processes in porous media occur in a variety of environmental, biological or industrial systems. The correct understanding of these processes is important for applications that range from kilometre scale

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problems (e.g. ground water management, contaminant spreading, petroleum industry, geothermal energy or CO_2 storage in geo-reservoirs, etc.) to millimetre or micrometre scale problems (e.g. pharmacokinetics, fuel cells, etc.). Many of these applications involve two, or three fluid phases, where mass transfer processes through the interfaces take place and involve changes in phase compositions.

A very recent problem dealing with two phase flow is the storage of CO_2 in deep saline aquifers. The CO_2 storage (CCS) in geological formations is one technology that can be used to reduce the greenhouse gas emissions [2–4]. After injecting the CO_2, four main trapping mechanisms in the storage formation have been identified [2]: 1) structural and stratigraphic trapping; 2) capillary or residual trapping; 3) solubility trapping; and 4) geochemical trapping. In order to increase the CO_2 storage efficiency in deep geological formations, injection strategies have to be optimized and a correct assessment of the CO_2 plume development is necessary. It is assumed that the size of the CO_2-brine interface determines the rate of dissolution of CO_2 into the brine (solubility trapping). Thus, an increase in the interfacial area would increase the dissolution of CO_2. In general, the interfacial area is expected to increase during the injection of CO_2 due to mixing, spreading and dispersion. However, the real plume development has to be determined experimentally in the laboratory and in the field, and with the help of numerical models. Standard multiphase models consider relations between capillary pressure and saturation and ignore the interfacial area between fluids. Recent advances in experimental setups and modelling approaches try to overcome this limitation. Currently there is very limited experimental data which show the pressure-saturation-interfacial area relationship for both drainage and imbibition. No experimental data is conclusive for the verification of theoretical model predictions which suggest that there are different interfacial areas for drainage and imbibition [5]. Most of the available relations have been derived from pore network models.

For CO_2 storage, the main questions to be answered are: what is happening to the CO_2 in the subsurface and how can it be monitored during and after injection? Monitoring techniques (e.g. tracers, well logs, seismic profiling, time-lapse 3D seismic imaging, soil and water chemistry, electrical and electromagnetic techniques, etc.) have been applied in the oil industry and for enhanced oil/gas recovery projects, where the timing of CO_2 injection relative to production is vital for the success of the operation. Nevertheless, direct techniques for time-dependent monitoring are limited in availability at present. Therefore, new tools, capable of describing and characterizing the spatial and temporal evolution of the plume and its interface in the reservoir are required.

Conventional tracer tests with water soluble tracer substances are useful for characterizing the reservoir, finding the flow and transport parameters, identifying possible leakage passages and predicting the integrity of the well. A new class of reactive tracers, termed as kinetic interface sensitive (KIS) tracers has been proposed [6]. These tracers have the potential to characterize the interfacial areas between supercritical CO_2 and brine and may thus provide additional information on: the effect of pressure stimulation on mixing; plume spreading, characterization of interfacial area and area change; identification of fingering effects; estimation of residual $scCO_2$ saturation; assessment of storage capacity and effectiveness; optimization of operational strategies, management of injection wells. The results of the first laboratory experiments are promising. To date, however, no model exists, which couple the prediction of the interfacial areas with the expected behaviour of KIS tracers.

In contrast to partitioning tracers, which are used to quantify the amount of saturation of immiscible hydrophobic phases (e.g. NAPLs or CO_2) in porous multiphase systems, KIS tracers exploit the reaction kinetics of a hydrolysis reaction at the interface for describing the interface development with time. Further details on tracer development and target molecular design can be found in Schaffer et al. (2012) [6]. The basic concept of these tracers can be summarized as follows: 1) the tracer is injected together with the CO_2 in the brine saturated aquifer; 2) the tracer adsorbs and saturates the interface; 3) the tracer reacts at the interface with water to highly water soluble reaction products; and 4) the reaction products can be measured in the water phase. The larger the interface (reaction surface) between both phases, the higher is the mass of the reaction products in the water phase. Thus, it is possible to establish a connection between time, concentration in water phase, and interfacial area size.

The focus of this work is to create the first mathematical model that is able to describe the behaviour of KIS tracers in two-fluid-phase porous media systems (CO_2-brine) and to account for the fluid-fluid interfacial areas. The aim is to use numerical modelling to design better tracers, experimental setups and better injection strategies capable of maximizing the interfacial area and capable of increasing the long-term trapping effectiveness.

2 Mathematical Model

2.1 Extension of the Two-Phase Flow Standard Model

The standard approach to model multi-phase flow in porous media is based on the extended Darcy's law:

$$v_\alpha = -K \frac{k_{r\alpha}}{\mu_\alpha} \left(\nabla p_\alpha - \rho_\alpha g \right), \tag{1}$$

where v_α is the apparent velocity of the phase α, K is the intrinsic permeability, $k_{r\alpha}$ is the relative permeability, μ_α is the dynamic viscosity, p_α is the pressure, ρ_α is the density and g is the gravitational acceleration. The conservation of mass in a multiphase flow system with respect to the volume is then written:

$$\frac{\partial \left(S_\alpha \phi \rho_\alpha \right)}{\partial t} - \nabla \cdot \left(\rho_\alpha K \frac{k_{r\alpha}}{\mu_\alpha} \left(\nabla p_\alpha - \rho_\alpha g \right) \right) - \rho_\alpha q_\alpha = 0, \tag{2}$$

where S_α is the saturation of phase α, ϕ is the porosity.

The classical coupling relations in a two phase flow porous medium system are:

$$S_w + S_n = 1, \tag{3}$$

$$p_n - p_w = p_c, \tag{4}$$

where p_c represents the capillary pressure, (w) wetting, (n) non-wetting phase.

A more fundamental approach of the two-fluid-phase flow in porous media can be derived from the thermodynamic principles. The movement of phases or interfaces is controlled by the gradient in the Gibbs free energy [7]. This interfacial area-based model is, indeed, able to describe the hysteretic behaviour of the classical model as well as kinetic interphase mass and energy transfer in a physically based way [1], [8], [9].

$$\tau_\alpha = \phi S_\alpha \rho_\alpha \left(\nabla G_\alpha - g\right), \tag{5}$$

$$\tau_{\alpha\beta} = \phi a_{\alpha\beta} \Gamma_{\alpha\beta} \left(\nabla G_{\alpha\beta} - g\right). \tag{6}$$

Here the τ_α and $\tau_{\alpha\beta}$ represent friction forces applied on phase α or interface αβ, G_α is the Gibbs free energy density, $a_{\alpha\beta}$ is the specific interfacial area, $\Gamma_{\alpha\beta}$ is the mass density and $G_{\alpha\beta}$ is the Gibbs free energy density of the αβ- interface. Considering that the medium is non-deformable, fluids are incompressible, interfacial mass density $\Gamma_{\alpha\beta}$ is constant, the influence of the solid on the interface is negligible and following the second law of thermodynamics as shown by [7] results:

$$\frac{\partial\left(a_{\alpha\beta}\right)}{\partial t} + \nabla \cdot \left(a_{\alpha\beta} v_{\alpha\beta}\right) = E_{\alpha\beta} \quad \text{, with} \qquad v_{\alpha\beta} = -K_{\alpha\beta} \cdot \nabla a_{\alpha\beta} \tag{7}$$

where $E_{\alpha\beta}$ is the rate of production of specific interfacial area.

2.2 *Specific Interfacial Area*

The measurement of interfacial area, $a_{\alpha\beta}(S_w, p_c)$ is a hard task especially for non-isothermal models where the solid phase has to be also taken into account. Most of the literature describes the calculation of the interfacial area by means of pore-network models. The pore network models are a very useful tool to get an insight in the fundamental understanding of the physics of flow and transport in porous media. The recent improvements in the imaging techniques such as X-ray computed tomography (CT) and magnetic resonance imaging (MRI), lead to more detailed information about the structure of the porous media. The basic idea of the pore network theory is to create a simplified network of pore geometries while preserving the essential features of the void spaces. Joekar Niasar et al. (2010) [15] suggested a bi-quadratic relationship between interfacial area, capillary pressure and fluid saturation:

$$a_{\alpha\beta}(S_w, p_c) = a_{00} + a_{10}S_w + a_{01}p_c + a_{11}S_w p_c + a_{20}S_w^2 + a_{02}p_c^2 \qquad (8)$$

A different formulation of the $p_c - S_w - a_{wn}$ quadratic surface which prevents negative values in the capillary pressure and saturation can be done in the form:

$$a_{\alpha\beta}(S_w, p_c) = a_0 \cdot (S_w)^{a1} \cdot (1 - S_w)^{a2} \cdot (p_c^{\max} - p_c)^{a3} \qquad (9)$$

This formulation has the advantage that it keeps the capillary pressures and saturations within the physical range, therefore, being more realistic. Figure 1 shows the comparison of the two approaches to represent $p_c - S_w - a_{wn}$ surfaces.

Table 1 reviews the coefficients used in the literature for macroscale modelling of capillary pressure-saturation-interfacial area by: 1) Niessner and Hassanizadeh (2008) [1] (Figure 1a), 2) Joekar Niasar et al. (2008) [10], 3) Ahrenholtz et al. (2011) [8], 4) new approach of Joekar-Niasar.

Table 1 Coefficients for the capillary pressure-saturation – interfacial area in literature

	a_{00} (m^{-1})	a_{10} (m^{-1})	a_{01} (m^{-1} Pa^{-1})	a_{11}(m^{-1} Pa^{-1})	a_{20}(m^{-1})	a_{02}(m^{-1} Pa^{-2})
1	-313.6	5535	0.085	-3937	-0.307	-5.0E-06
2	849	3858	-0.224	-3992	0.006	1.283E-05
3	-71.64	4.103E+03	0.3626	-0.4505	-3.733E+03	-3.514E-05
4	5.630	0.4797	-7.692E-04	-4.376	1.606E-04	3.169E-08

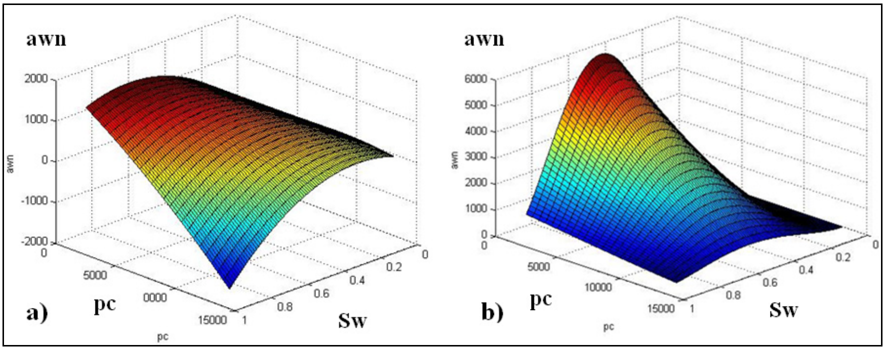

Fig. 1 Capillary pressure - saturation - specific interfacial area ($p_C - S_w - a_{wn}$) surfaces according to a) Niessner and Hassanizadeh (2008) [1] and to b) equation (9), which maintains the capillary pressure and saturations in physical ranges

2.3 Capillary Pressure

Generally, the capillary pressure–saturation relationship in standard two-phase models is given by one of the following formulations as a function of saturation: Brooks-Corey, Van Genuchten or a linear law e.g. Helmig (1997) [11]. In the following the Brooks-Corey approach is going to be used:

$$p_c(S_w) = p_d S_e^{-\frac{1}{\lambda}} \quad \text{with} \quad S_e = \frac{S_w - S_{wr}}{1 - S_{wr}} \tag{10}$$

However, the capillary pressure is a function not only of saturation, but also a function of interfacial area: $p_c = p_c(S_w, a_{wn})$ and it has been shown [10] that it is not unique.

2.4 Relative Permeability

According to Niessner and Hassanizadeh (2008) [1] the dependence of relative permeability on the interfacial area is small and therefore standard formulations should be sufficient. Based on the *Burdine-Brooks-Corey* approach we can write the relative permeability relations:

$$k_{rw} = S_e^{\frac{2+3\lambda}{\lambda}}, \text{and} \quad k_{rn} = (1 - S_e)^2 \left(1 - S_e^{\frac{2+\lambda}{\lambda}} \right) \tag{11}$$

2.5 KIS Tracer Modelling at the Interface

The governing equation for KIS tracer migration in the two-phase porous media system is:

$$\frac{\partial (S_n \phi C_n^T)}{\partial t} - \nabla \cdot (C_n^T v_n + D_n^T \nabla C_n^T) - Q_{n \to w}^T = 0, \tag{12}$$

where D_α^T is the macroscale dispersion coefficient, $Q_{n \to w}^T$ is the interphase mass transfer rate of tracer T from phase n (CO_2) to w (brine). D_α^T is the sum of the mechanical or kinematic dispersion and the effective diffusion coefficient. For the numerical modelling of the interfacial sensitive tracers several approaches could be considered: effective rate coefficient [12], local equilibrium assumption, dual domain approach, or non-equilibrium approach [9]. The main targets in the molecular design of the KIS tracer are substances which decay in the non-wetting phase following the linear zero order reaction kinetics of the hydrolysis reaction. This makes the interphase mass transfer dependent on the interfacial area:

$$Q^T_{\alpha\to\beta} = k^T_{\alpha\to\beta} a_{\alpha\beta} , \tag{13}$$

where $k^T_{\alpha\to\beta}$ is the mass transfer rate coefficient.

3 Numerical Simulations

We perform a simple numerical experiment to simulate the evolution of interfacial area in a column. The results could be used later for comparisons with laboratory experiments. Compressed air is injected into a fully water saturated porous medium. The pressure at the inlet is kept constant at 200 kPa. The outlet pressure is controlled and stays at 100 kPa. (Air represents the non-wetting phase and water is the wetting phase.) The domain is 30 cm long and has a 3 cm diameter. The interfacial area is calculated with the formulation from equation (9) having a0=1, a1 = 2, a2 = 2, a3 = 1.2 (see Figure 1b). These parameters should correspond to medium-sized sands. Intrinsic permeability is K=1.0e-12 m^2, porosity 0.2. Brooks Corey parameters from equation (10) are p_d =1000, λ=2. Initial conditions are S_w=1.0, p_w=100 kPa.

The system of equations is solved with the free open-source numerical toolbox DuMux (www.dumux.org)[13] . For the spatial discretization the box method is used (see [11]), which combines the advantages of finite element and finite volume methods, being locally mass conservative and applicable to unstructured grids. The time discretization uses the fully implicit Euler scheme known for its stability.

The results (Figure 2) depict the spatial and temporal distributions of the non-wetting phase saturation and the specific interfacial area. Immediately after the air begins to enter the domain, the interfacial-area has a sharp increase which continues until the air front reaches the outlet (Figure 2(a)(b)). The Dirichlet boundary at the outlet has an accumulation-like effect, producing an increase of non-wetting phase saturation in the whole domain. However, the interfacial area is beginning to decrease as the water is completely pushed out from the porous medium (Figure 2(c)).

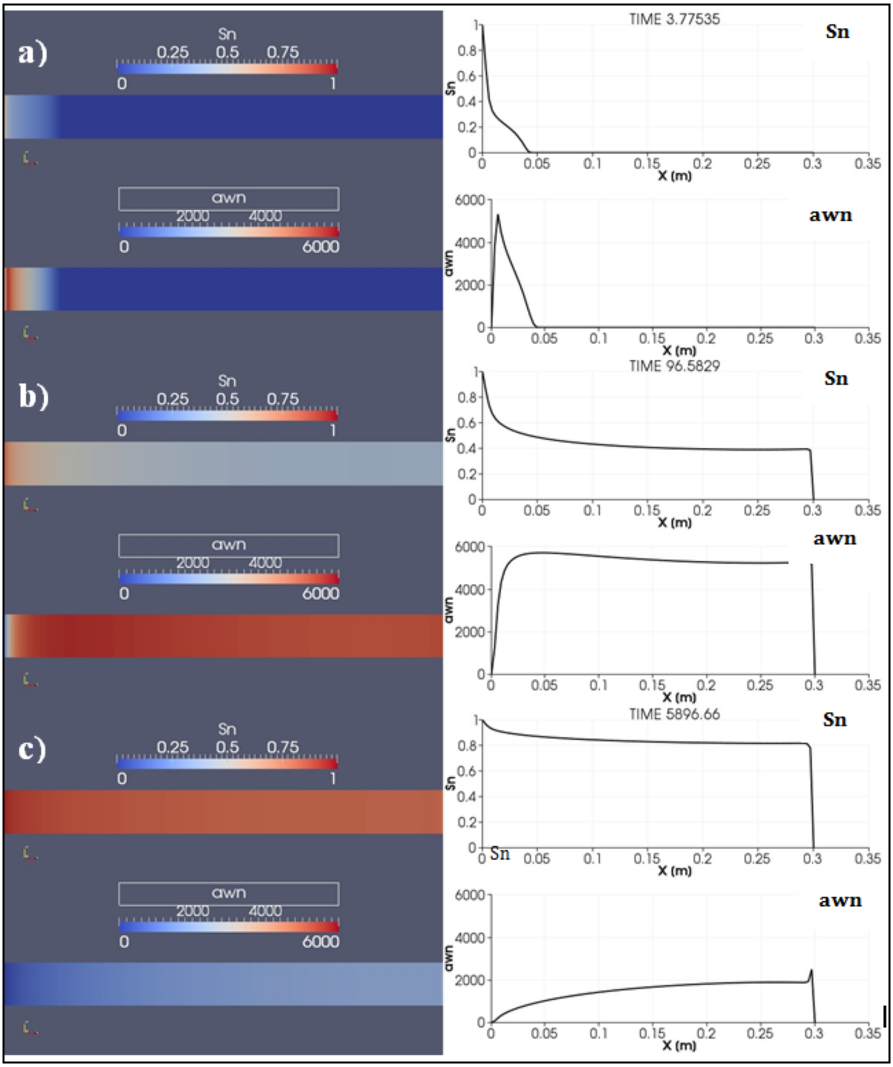

Fig. 2 Column experiment: spatial distribution of non-wetting saturation (upper-left), interfacial area (lower left) and plot over line passing through points A1(0.0, 0.015)-A2(0.30, 0.015). a) Air begins to infiltrate into the column; b) Air reaches the outlet and starts to accumulate in the domain; c) interfacial area decreases as water is pushed out of the column.

4 Conclusions

We have shown a first mathematical model that accounts for interface sensitive tracer transport in two-fluid-phases in porous media has been demonstrated.

The main features of the models are that it includes additional balance equations for the interfaces.

The relations for capillary pressure – saturation – specific interfacial area per unit volume of porous medium $p_c - S_w - a_{wn}$ were calculated according to pore network modelling results. The interfacial area is represented with a quadratic surface and accounts for non-unique capillary pressure values.

The model is aimed to provide an extension to the laboratory work of developing kinetic interface sensitive tracers [6], [14]. The amount of interfacial area will be later compared with the laboratory results and could be used as a validation for pore network models. Future work includes constructing and running dynamic laboratory experiments and development of the system of equations towards a multi-compositional approach, and of the numerical simulator. The multi-compositional model will be able to handle the rate of dissolution of CO_2 into water and of water in the CO_2 phase together with the hydrolysis reaction of tracer at the interface.

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